

TRACE ELEMENT MASS BALANCE
AROUND A COAL-FIRED STEAM PLANT*

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1. Introduction

Toxic elements are present in trace quantities in coal and other fossil fuels. Since the quantities of these fuels consumed each year are enormous, the associated quantities of potentially harmful toxic elements are also appreciable. For example, assuming 600 million tons of coal burned per year in the United States, with average concentrations*** for Hg of 0.10 ppm, Pb-20, Cd-0.4, As-5, Se-5, Sb-4, V-25, Zn-200, Ni-100, Cr-20, and Be-2, the corresponding tonnages of the elements are: Hg-60, Pb-12,000, Cd-240, As-3000, Se-3000, Sb-2400, V-15,000, Zn-120,000, Ni-60,000, Cr-12,000, and Be-1200.

An appreciable fraction (62%) of the coal consumed is burned at central power stations, so it is important to know the fate of potentially hazardous trace elements at such plants. The purpose of this work is to determine the fate of trace elements in coal associated with generation of electricity at a large central power station. The study involves two complementary activities: (1) a mass balance for trace elements through the plant as obtained by in-plant sampling, and (2) measurements of the elements in the surroundings to estimate the effect of emissions on the concentration of toxic elements in air, soil, plant life, and in the water, sediment, and biota of the stream receiving the ash pond runoff. This paper deals with the in-plant portion of the work, which is a collaborative effort between ORNL and TVA.

The power station at which the study was made is the Thomas A. Allen Steam Plant in Memphis, Tennessee, which has an 870 MW(e) peak capacity from three similar cyclone fed boilers. The plant is part of the TVA power system, and it was chosen because the Number 2 Unit was being renovated with addition of a new Lodge Cottrell electrostatic precipitator so the TVA Power Production Division test sampling crew were available to help sample during compliance testing of the precipitator.

2. Sampling and Methods of Analysis

Figure 1 shows the sampling points on a schematic of the Number 2 Unit. Samples taken at locations Number 1 and 2 were composite samples of the coal entering the boiler, and of the slag material leaving the boiler, respectively. At location Number 3 the inlet air being supplied to the boiler was sampled. At locations 4 and 5 a series of samples were taken isokinetically at various locations in the ducts before and after the electrostatic precipitator, respectively; and at location 6 a series of samples were taken isokinetically in the stack at approximately 82 m above ground level.

The large size of the ducts being sampled required specially fabricated sampling

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*** These concentrations are representative of values measured for coal burned at the Allen Steam Plant.

probes and special probes equipped with forward-reverse pitot tubes for determining isokinetic sampling rates. Figure 2 shows how the sampling probe was constructed. The sample is drawn through an alundum thimble at a predetermined isokinetic sampling rate. This thimble is followed by a Gelman fiberglass filter paper holder which collects particles as small as 0.1μ . This is essentially the standard ASTM method for sampling gases for particulates.¹ These filters are then followed by the cold trap to bring the flue gas through the dew point very quickly and collect all materials which will condense in a dry trap. Because of the very high concentration of moisture in the flue gas it was necessary to add a dropout glass jar following this cold trap to prevent loss of the condensate. The cold trap and condensate dropout jar were used in an attempt to trap mercury and other condensable vapors from the flue gas sample.

Two probes were fabricated for sampling the precipitator inlet, one for the precipitator outlet and one for the stack. By limiting the number of test points at each plane in the precipitator outlet the average sampling time required to complete a test was about 280 to 300 minutes. The types and numbers of samples collected for each complete run are shown in Table 1. The total number is 24 distinct samples for each complete test run.

Table 1. Types and numbers of samples

Composite Coal Sample - 1
Composite Slag Tank Sample - 1
Precipitator Inlet - 6 thimbles, 2 cold traps, 2 glass papers
Precipitator Outlet - 4 thimbles, 1 cold trap, 1 filter paper
Stack Sample - 2 thimbles, 1 trap, 1 glass paper
Inlet Air - 1 thimble and 1 glass paper

Although the plant is designed to operate at 290 MW per unit, a 240 MW load was chosen for these tests because it was felt that this load could be maintained without interruption during the 5-hour sampling time required to secure our samples. The consumption of coal at this power level is 82.5 tons per hour on a dry weight basis. Sampling of the coal and slag was performed by compositing samples obtained periodically during the course of the test. From the weight of fly ash material collected in the ASTM filter system, the total air volume passed through the thimble, and the velocity of air passing through the system, the total particulate flow rate was calculated. In all, four runs were made, 1 reference test, and 3 for mass balance (runs 5, 7, and 9). A gas velocity traverse was made in the precipitator inlet and outlet ducts just prior to each mass balance run to determine isokinetic sampling rates for each sampling position.

The reference test was performed using the standard ASTM method for determining grain loadings to electrostatic precipitators. This test was used to verify the adequacy of the number of samples secured for mass balance calculations. Comparison of grain loading calculations using TVA standard probes and ORNL fabricated probes show the mass balance samples are, indeed, representative.

Analysis of the samples for elemental constituents was performed using instrumented neutron activation analysis (NAA) and spark-source mass spectrometry (SSMS).² In addition, the many Hg determinations were made by flameless atomic absorption (AA).

The NAA technique involved irradiating each dry homogenized sample (0.01 to 0.2 g) in a sealed plastic vial. This vial was placed in a "rabbit" together with

Au and Mn flux monitors and irradiated in the Oak Ridge Research Reactor for a period varying from a few seconds (for short lived radioactive products), to 20 minutes. After irradiation the samples were removed and counted at various set decay times using a Ge(Li) detector and a nuclear-data PDP-15 analyzer computer system. Using programs developed at ORNL, these counting data were processed, and x-ray peaks identified, absolute activities calculated, and from the flux measurement and known nuclear parameters, the $\mu\text{g/g}$ of each element found was calculated. Results in all cases have a 5-10% uncertainty assignment. The entire process is nondestructive in that no chemical treatment is performed, so there is only a minimal chance of sample contamination or loss.

The flameless atomic absorption method has a reproducibility of about 2% or better for homogeneous specimens. Checks³ between AA and NAA (with radiochemical separation after irradiation) and isotope dilution spark source mass spectroscopy on thoroughly homogenized tuna fish and Bureau of Mines round-robin coal specimens indicate good agreement between the methods. ($0.425 \pm 0.9\%$, $0.45 \pm 3.5\%$, and $0.45 \pm 4.4\%$ for tuna by AA, NAA, and SSMS, respectively, and 1.004 is the average ratio of NAA to AA results for 5 coal samples.) These results indicate that the technique used in sample preparation for AA did not result in mercury losses since the NAA method is not subject to losses of this type.

Spark-source mass spectrometry (SSMS) is also a multi-element technique; conventionally the data obtained are semi-quantitative and the results have an uncertainty of $\pm 50\%$ or less. If the stable isotope dilution technique is performed, the SSMS can be $\pm 3\%$. This latter technique was used for a few elements: Pb, Cd, and Zn as noted in the tabulations of results. NAA and SSMS complement each other quite well, and those elements for which one technique has poor sensitivity can usually be measured by the other.

3. Mass Balance Results

A mass balance for the various elements was calculated using the following equations:

$$Q_C(A) = C_C(A) \times (\text{g coal/min}) \quad (1)$$

$$Q_{P.I.}(A) = C_{P.I.}(A) \times (\text{g fly ash/min}) \quad (2)$$

$$Q_{S.T.}(A) = C_{S.T.}(A) \times (\text{g ash in coal/min} - \text{g fly ash to precipitator/min}) \quad (3)$$

for balance:

$$Q_C(A) = Q_{P.I.}(A) + Q_{S.T.}(A) \quad (4)$$

$$\text{percent imbalance} = \frac{Q_{P.I.} + Q_{S.T.} - Q_C}{Q_C} \times 100 \quad (5)$$

$Q_C(A)$, $Q_{P.I.}(A)$ and $Q_{S.T.}(A)$ are the flow rates of element A in g/min associated with the coal, precipitator inlet fly ash, and slag tank solids, respectively, and $C_C(A)$, $C_{P.I.}(A)$ and $C_{S.T.}(A)$ are the corresponding concentrations of element A in the coal, the fly ash collected in the precipitator inlet, and the slag tank solids. The flow of trace elements into the plant with suspended particulates in inlet air was negligible. We were unable to measure the total solids flow from the slag tank because of the nature of this discharge. (Every four hours the slag tank residue is washed out to the ash pond with 2-4 hundred thousand gallons of water.) For this reason we estimated the slag tank discharge as the difference between ash flow rate in the coal and the total fly ash flow rate. Presuming that this assumption is valid, that the sampling was complete and representative, and that

the analyses are correct, the condition for balance is given by equation 4. To test this we have calculated a percent imbalance from experimental results by equation 5. Also, the precipitator efficiency for an element was calculated by

$$\text{Precipitator efficiency} = \frac{Q_{P.I.}(A) - Q_{P.O.}(A)}{Q_{P.I.}(A)} \times 100 \quad (6)$$

The results of the mass balance calculations for 8 major elements and 22 minor elements for run 9 are given in Tables 2 and 3, together with the corresponding concentrations in the coal, precipitator inlet and outlet fly ash, and in the slag tank solids. A complete tabulation of results for all three runs is given in a progress report of the project⁴ and this includes some data for 57 elements.

In general, agreement between the two analytical methods is reasonable. There is a consistent negative imbalance, the average of which was -26% and -16% for NAA and SSMS results, respectively, for the major elements and -1% and -18% for the minor elements. In the averages for minor elements we have excluded the results for Hg and As. In view of the assumptions necessary and the difficulty of obtaining truly representative samples the balance is satisfactory for most elements. Notable exceptions are elements which can be present in a gaseous form. One may be arsenic (Table 3) and another is mercury which is discussed below. One reason for the consistent negative imbalance could be that fly ash samples were taken under steady state conditions. Two operations were not investigated and these might account for this imbalance. The air heaters are cleaned pneumatically once per 8-hour shift, and soot is blown from the boiler tubes about two times per shift. If this material were measured it would increase the average fly ash flow rate ($Q_{P.I.}$). It is not known whether or not these operations can account for a significant percentage of the trace elements. Future in-plant sampling will include these two operations.

As in the case of the slag tank there was no way to quantitatively measure the precipitator residue flow rate. These residues are slurried with water and flushed continuously to the ash pond. However, for all of the elements except selenium the precipitator was extremely efficient (> 95%) as calculated from the inlet and outlet fly ash concentrations using equation 6. The reason that selenium fails to be scavenged effectively is not known and certainly warrants investigation. One possibility is that part of the selenium is in a volatile state but is readily adsorbed on particulates trapped by the alundum thimbles.

Mercury has been determined on virtually every sample (the filters, cold trap and slag tank water and residue). We are unable, however, to find the bulk of the Hg that we know is entering the system via the coal. From this we conclude that Hg is present in the stack gas as a vapor which we were unable to trap.

Table 4 gives all of the values obtained for Hg in coal which range from .057 to .198 ppm, but most values are in the range of 0.07 ppm. Our attempt at a Hg balance for runs 5 and 9 is shown in Table 5. From these numbers it is clear that very little mercury (~ 12%) remains with the slag and fly ash particles. The cold trap was not effective in trapping Hg vapor (~ 11%). The results are in qualitative agreement with those of Billings and Matson,⁵ except that these authors were able to collect the Hg in the gas phase. Their data shows that most of the Hg is in the gas phase which can also be implied from our results.

Recently, we returned to the Allen plant and sampled the flue gas using a four impinger train with a pre-scrubber of sodium carbonate to remove the acid gases, followed by three impingers charged with iodine monochloride solution. Preliminary results show that mercury was collected and quantities detected were of the expected magnitude based on Hg concentrations in the coal which we had measured previously. This technique will be used for the Hg balance at the next in-plant sampling.

Table 2. Elemental concentrations and mass balance results for a number of major elements measured for run 9

Element	Method	Concentration (ppm unless otherwise indicated)				Mass Flow (g/min)				Precipitator Efficiency (%)	
		Coal		P.O. ^a		Coal	S.T. ^a	P.L. ^a	Imbalance (%)		
		S.T. ^a	P.L. ^a	P.O. ^a							
Al	NAA	1.06%	6.6%	6.9%	3.5%	1.3 × 10 ⁴	7.2 × 10 ³	3.4 × 10 ³	-18	68	98
	SSMS	1%	5%	15%	10%	1.3 × 10 ⁴	5.5 × 10 ³	7.3 × 10 ³	-1	190	97
Ca	NAA	0.38%	2.7%	1.4%	0.49%	0.47 × 10 ⁴	3.0 × 10 ³	6.8 × 10 ²	-22	9.5	99
	SSMS	0.5%	3%	3%	1%	0.6 × 10 ⁴	3.3 × 10 ³	1.5 × 10 ³	-20	19	99
Fe	NAA	1.3%	10.1%	9.3%	23.5%	1.6 × 10 ⁴	1.1 × 10 ⁴	4.5 × 10 ³	-3.1	460	90
	SSMS	2%	10%	10%	10%	2.5 × 10 ⁴	1 × 10 ⁴	5 × 10 ³	-40	190	96
K	NAA	0.22%	0.95%	1.65%	1.28%	0.27 × 10 ⁴	1.0 × 10 ³	8.0 × 10 ²	-33	25	97
	SSMS	0.06%	0.5%	0.7%	0.2%	0.07 × 10 ⁴	5 × 10 ²	3 × 10 ²	+14	4	99
Mg	NAA	0.17%	0.41%	0.53%	0.88%	0.21 × 10 ⁴	4.5 × 10 ²	2.7 × 10 ²	-66	17	94
	SSMS	0.15%	0.7%	0.4%	0.4%	0.18 × 10 ⁴	8 × 10 ²	3 × 10 ²	-39	8	98
Mn	NAA	54	418	323	550	67	46	16	-7.5	1.1	94
	SSMS	100	1000	700	500	130	110	34	11	1	97
Na	NAA	0.069%	0.32%	0.7%	0.28%	860	350	340	-20	5.5	98
	SSMS	0.03%	0.2%	0.3%	0.2%	370	220	150	0	4	97
S	NAA	5.1%	30%	30%	10.5%	6.4 × 10 ⁴	3.3 × 10 ⁴	1.5 × 10 ⁴	-24	190	99
	SSMS	5%	30%	30%	10%	6.3 × 10 ⁴	330	180	-43	4.9	97
Ti	NAA	710	3000	3700	2500	890	220	240	-48	2	99
	SSMS	700	2000	5000	1000	880	220	240	-43	2	99

^aS.T., P.L., and P.O. are abbreviations for slag tank solids, precipitator inlet, and precipitator outlet, respectively.

Table 3. Elemental concentration and mass balance results for a number of minor elements measured for run 9

Element	Method	Concentration (ppm)				Mass Flows (g/min)			
		Coal		P.O. ^a		S.T. ^a		P.I. ^a	
		Coal	S.T. ^a	P.I. ^a	P.O. ^a	Coal	S.T. ^a	P.I. ^a	Inbalance (%)
As	NAA	3.8	0.5	46	50	4.7	0.05	2.2	-52
	SSMS	5	2	40	20	6.2	0.2	2	-64
Ba	NAA	79	600	1700	100	99	66	83	-11
	SSMS	100	300	<10	<10	130	33	83	+8.5
Be	SSMS	<5	<10	17	<6.3	<1.1	<1.1	0.83	0.014
	ID ^b	0.47	~3	5.8	0.31	0.59	0.31	0.33	0.11
Cd	SSMS	0.5	2	<10 - 20	7	0.63	0.22	<0.5 - 1.0	<96 ^c
	SSMS	0.5	2	<10 - 20	7	0.63	0.22	<0.5 - 1.0	91
Co	NAA	3.3	19	25	4.1	9	4.4	3.4	-19
	SSMS	7	40	70	40	9	4.4	3.4	-13
Cr	NAA	21	180	356	300	26	20	17	42
	SSMS	30	<200	70	40	37	<22	3.4	0.6
Cs	NAA	1.5	8	21	4	1.9	0.88	1.02	0
Cu	SSMS	50	200	400	400	63	22	19	-35
Eu	NAA	0.17	1.4	1.8	0.21	0.21	0.15	0.09	14
	SSMS	~1	0.09	0.043	~1	~1	0.0099	0.0021	-85
Hg	AA	0.063	0.09	32	6.3	6.3	4.6	1.5	-3
La	NAA	5.0	42	32	200	31	22	15	19
	SSMS	~10	200	300	200	25	8.8	9.7	-26
Li	NAA	25	200	300	200	31	22	15	0.4
Mo	NAA	20	80	200	20	25	55	24	0.04
	SSMS	<100	500	500	1000	<130	55	24	2
Ni	SSMS	7.4	~4	149	9.25	0.42	8.60	12	92
Pb	ID ^b	<20	3	250	100	<25	0.3	12	-3
	SSMS	<1	<0.2	3.2	<0.75	<0.75	<0.02	0.2	0.2
Sb ^d	NAA	8	7	10	10	8	0.8	0.5	0.2
	SSMS	3.2	22	25	10	4.0	2.4	1.2	0.02
Sc	NAA	3.2	14	<32-48	760	4.0	1.5	<1.5-2.3	-10
Se	NAA	3.2	14	<32-48	760	4.0	1.5	<1.5-2.3	<-25 to -5
	SSMS	6	20	200	7.5	2.2	1.0	0.83	1.4
Sn ^e	SSMS	20	200	20	20	25	20	1.4	-58
	SSMS	20	200	20	20	25	20	1.4	0.4
Th	NAA	3	20	18	3.7	2.2	0.87	1.9	-14
	SSMS	<2	2	40	30	<2.5	0.2	1.9	-17
Ti	NAA	1.67	14	17	7	2.1	1.5	0.83	11
U	NAA	21	125	200	63	26	14	9.7	0.014
V	SSMS	30	100	350	100	37	11	17	0.12
	ID ^b	94	~20	1500	117	117	2.1	86	-9
Zn	SSMS	85	100	3000	900	110	11	150	-24
	SSMS	85	100	3000	900	110	11	150	1.7

^aS.T., P.I., and P.O. stand for slag tank solids, precipitator inlet, and precipitator outlet, respectively.^bData obtained by isotope dilution mass spectrometry for composite samples from runs 5 and 9.^cPrecipitator efficiencies calculated on the basis of P.O. by SSMS for run 9 and P.I. by ID from the composite sample runs 5 and 9.^dRun 5 data.^eRun 7 data.

Table 4. Hg in coal as determined by atomic absorption

Sample	Date	Hg(μ g/g)		
2 ECS 24	26 Jan	0.057		
5 CS 24 AM	28 Jan	0.064	0.063	
5 CS 24 PM	28 Jan	0.069	0.058	
7E CS 26 AM	31 Jan	0.198		
7E CS 26 PM	31 Jan	0.169	0.148	0.136
9E CS 16 AM	1 Feb	0.076	0.060	
9E CS 16 PM	1 Feb	0.060	0.058	
10E CS 19 AM	2 Feb	0.068		
10E CS 19 PM	2 Feb	0.073		
11E CS	3 Feb	0.060		

Table 5. Hg balance

Material	Average Flow g/day	Hg μ g/g	Hg Flow g/day
Run 5			
Coal	1.8×10^9	0.064	115
Ash (Slag)	1.43×10^8	0.07	10
Precipitator Inlet	0.96×10^8	0.04	4
H ₂ O to Ash Pond	2.9×10^9	0.003	9
Gas (Cold Trap)	4.3×10^{10}	0.0003	13
Run 9			
Coal	1.8×10^9	0.064	115
Ash (Slag)	1.58×10^8	0.09	14
Precipitator Inlet	0.70×10^8	0.043	3
H ₂ O to Ash Pond	2.9×10^9	0.001	3
Gas (Cold Trap)	4.4×10^{10}	0.0003	13

4. Fly Ash Particle Characterization

Figure 3 shows scanning electron photomicrographs of fly ash particles from the precipitator inlet and outlet and from the stack. The particles are predominantly spherical and there is considerable agglomeration of small particles (submicron size) to large ones. Also, there appears to be a fuzzy material present which might be a sulfur compound. Preliminary evidence for this is scanning electron microscope fluorescence analyses of some of the larger particles deposited from the precipitator inlet flue gas on the first stage of a Cassella cascade impactor. Figure 4 shows such an analysis. All of the fluorescence lines, except aluminum, can be attributed to the particles. Since the particles were collected on an aluminum foil the aluminum peak is due primarily to the foil. Upon ion etching by bombardment with argon ions, the sulfur peak decreased substantially indicating sulfur was present primarily on the surface of the particles. As one would expect, the preliminary evidence is that the fly ash particles are a complicated mixture of the elements.

Work is still in progress on determining the particle size distribution in the flue gases before and after the precipitator, and in the stack. Also, composition of fly ash as a function of particle size is in progress.

5. Conclusions

Trace element mass balance measurements around the Number 2 Unit of the coal-fired Allen Steam Plant in Memphis yielded a respectable balance for many elements. However, the results showed a consistent negative imbalance. This might be due to the fact that soot blowing and air heater cleaning operations were not taken into account in the sampling. Because the method of flue gas sampling was designed primarily to collect particulates efficiently, good balances were not obtained for elements forming volatile compounds. For example, more than 80% of the mercury entering with the coal is emitted with the flue gas as a vapor. The large imbalance for arsenic (-58%, Table 3) indicates that a substantial portion of this element is also in the vapor phase of the flue gas.

The electrostatic precipitator was very efficient (~98%) for most trace elements based on analyses of the fly ash particulate specimens collected from the precipitator inlet and outlet. An exception was selenium. Although a reasonable mass balance was obtained for this element (see NAA results, Table 3), it was not removed efficiently by the precipitator. This may indicate that a significant fraction of the material is in the vapor phase in the flue gas, and that it is being adsorbed in

passing through the alundum thimble filter used to sample the fly ash. Accounting more completely for the volatile trace elements such as Hg, Se, and As remains the most significant question still to be answered in future mass balance work.

6. Acknowledgements

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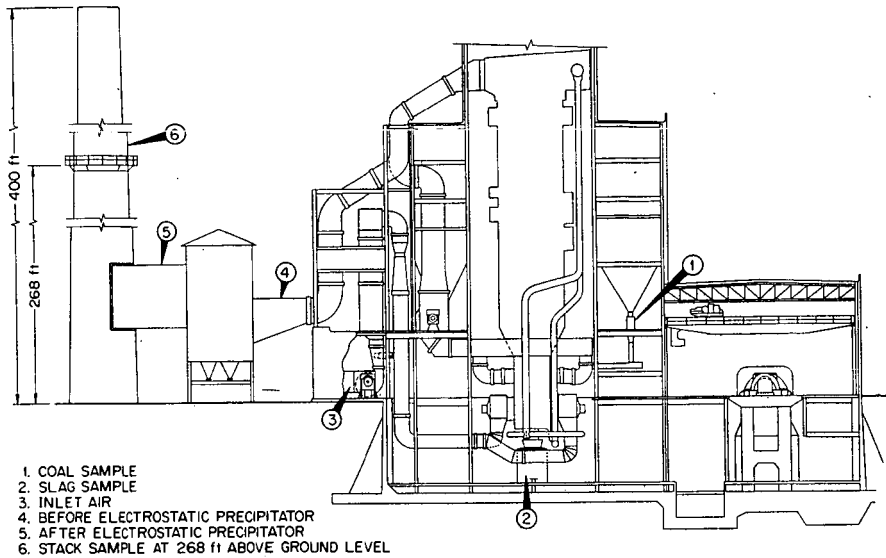


Fig. 1. Schematic of Number 2 Unit, Allen Steam Plant, Memphis.

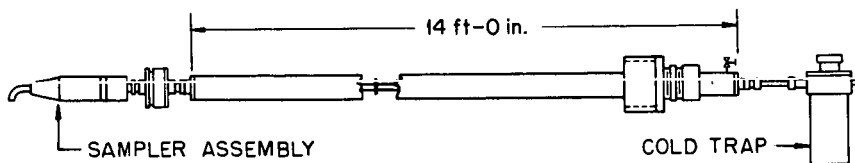


Fig. 2. Schematic of Sampling Probe Used for Mass Balance Study.

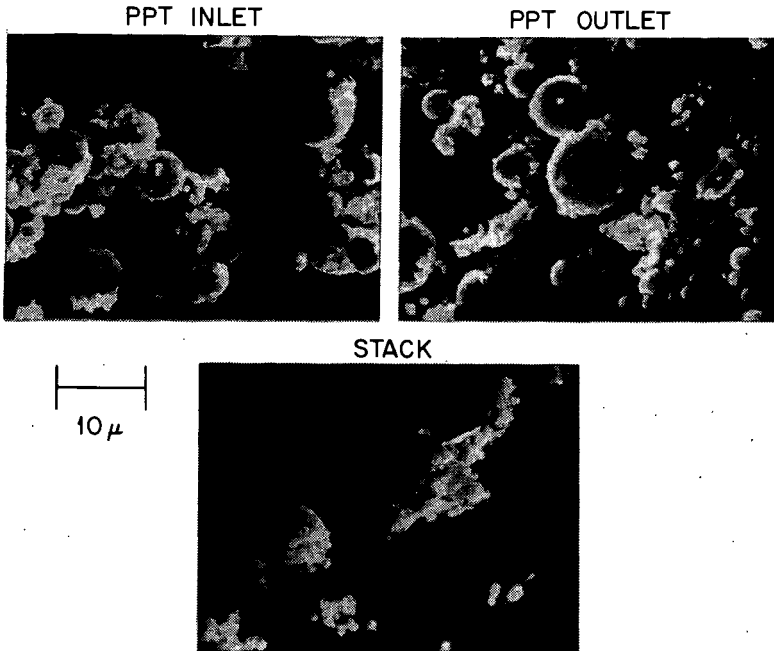


Fig. 3. Scanning Electron Photomicrographs of Fly Ash Particulates Collected on Alundum Thimbles Used to Sample the Precipitator Inlet and Outlet and the Stack.

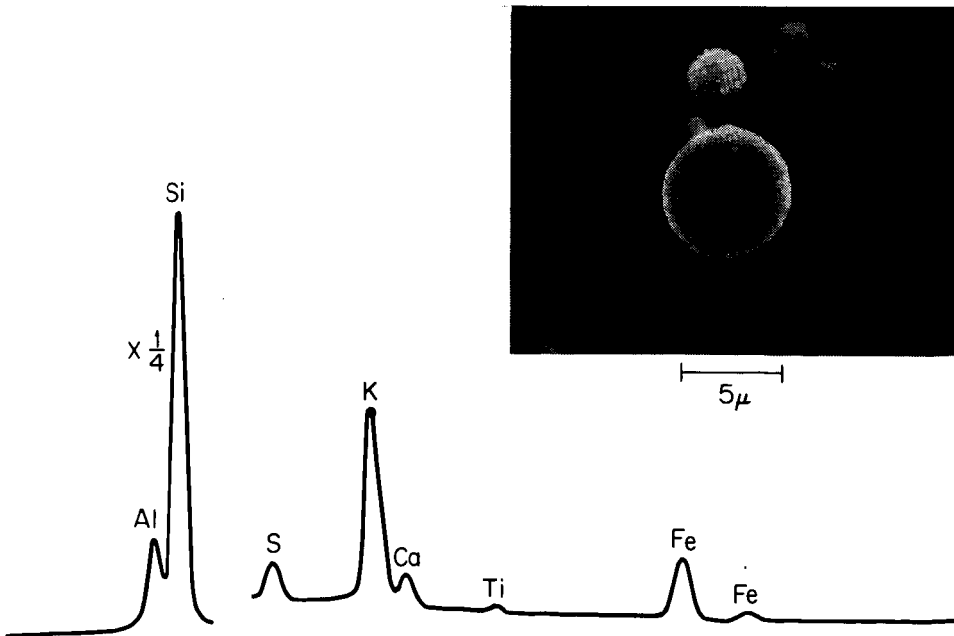


Fig. 4. Qualitative Fluorescence Analysis of a 5 μ Fly Ash Particle Trapped on the First Stage of the Cassella Cascade Impactor Used to Sample the Precipitator Inlet.